Intramolecular Dissociative Electron Transfers

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A significant amount of work has been carried out to characterize the activation/driving force relationships ruling dissociative electron transfers, i.e. those reactions in which ET and σ-bond cleavage are either concerted or stepwise.[1-3] Most processes were investigated by studying families of closely related compounds to better define the transition between concerted and stepwise mechanisms.[1-4] The investigated reactions were mostly heterogeneous or homogeneous intermolecular reductions. In the last 15 years the study of intramolecular electron transfer reactions in D-Sp-A molecules, in which a donor (D) and an acceptor (A) are separated by a molecular spacer (Sp), has provided a variety of information on how electrons are transferred through bonds and space.[5] In the case of dissociative electron transfers, however, much less is known. So far, the only published results concern the free energy dependence in systems in which A is C-Br and Sp is cyclohexyl.[6] Very recently, further data have been collected on other D-Sp-A systems, in which the acceptor moiety is a peroxide.[7] In this communication we will present data on the effects of varying the donor, the acceptor, or the spacer. It will be shown how relevant are the actual values of the reaction free energy, the intrinsic barrier, and the pre-exponential factor. The latter is particularly important because it contains the contribution of the electronic coupling between reactant and product states.

References

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